Kinetics of Hydrolysis of Di-μ-hydroxo-bis[nitrilotriacetatocobaltate(III)] to Diaqua(nitrilotriacetato)cobalt(III), and some Reactions of the latter with Non-metallic Substrates in Aqueous Solution

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The kinetic behaviour of di-μ-hydroxo-bis[nitrilotriacetatocobaltate(III)] on hydrolysis in acid solution gives evidence for two isomeric forms of different reactivity. The product, diaqua(nitrilotriacetato)cobalt(III), is reduced to cobalt(II) by hydrazine, hydroquinone, hydroxylamine, iodide, and thiosulphate in acidic solutions. With thiocyanate, replacement of ligand water occurs, and with nitrite, ligand water substitution occurs at pH 4·5, and reduction of cobalt(III) occurs at pH 5·6. Similarities in the rate constants for these reactions suggest that the formation of an inner-sphere complex with the substrate is rate determining. Sulphite also reduces the cobalt(III) complex, but here decomposition of a rapidly formed sulphitocobalt(III) inner-sphere complex appears to be the slow step.

THE aim of this investigation was to choose a cobalt(III) complex containing at least one ligand water molecule which could be substituted by easily oxidised ligands, and then to study the mechanism of decomposition of such derived complexes to cobalt(II) and the oxidised forms of the ligands. Because strongly complexing ligands, especially ammonia and related organic compounds, greatly decrease the reduction potential of cobalt(III), we investigated complexes with not more than two co-ordinated nitrogen atoms, and eventually chose diaqua(nitrilotriacetato)cobalt(III), $[Co(nta)(OH_2)_2]$, as a promising parent complex. The reduction potential between this complex and the corresponding cobalt(II) compound was found to be *ca.* 0·7 V which appeared to be sufficiently high. It was necessary to investigate the preparation and purification of this cobalt(III) complex in some detail because the original formulation of various cobalt(III)–nta complexes has since been disputed.

Mori *et al.*[1] described the preparation of three cobalt(III)–nta complexes in the solid state. These are the α and β forms which they considered to be isomeric forms of $K[Co(nta)(OH)(OH_2)]\cdot xH_2O$ ($x = 2$ for the α form, 3 for the β), and a third material, referred to as the 'diol complex,' of formula $K_2[(nta)Co(\mu\text{-}OH)_2Co(nta)]\cdot 6H_2O$. Subsequently, Smith and Sawyer[2] investigated the ^1H n.m.r. spectra of these complexes in aqueous solution, and concluded that the α form is a binuclear complex, either of the di-μ-hydroxo- or mono-μ-oxo-type and that the β form is indeed a mononuclear complex. We accept these conclusions, although our preparations of the β form always contained cobalt(II). There is no obvious steric reason against a di-μ-hydroxo-structure for the α form, and this type of structure occurs in other binuclear cobalt(III) complexes.[3] Hence, we prefer it to the alternative formulation as a mono-μ-oxo-complex, $K_2[(H_2O)(nta)Co(\mu\text{-}O)Co(nta)(OH_2)]\cdot 5H_2O$, examples of the latter type of bridge being rare in cobalt chemistry. Moreover, such a μ-oxo-complex, containing a water ligand *cis* to each cobalt(III) atom, would seem liable to ring closure giving the di-μ-hydroxo-form. Finally, we have shown by analysis that a compound prepared in the same way as Mori's 'diol complex' is a bis(nta) complex, $K[Co(Hnta)_2]\cdot 2H_2O$.

Although the β form is the conjugate base of the complex required for our redox studies, we found its purification troublesome and have chosen to prepare this mononuclear complex in solution, by acid hydrolysis

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[1] M. Mori, M. Shibata, E. Kyuno, and Y. Okubo, *Bull. Chem. Soc. Japan*, 1958, **31**, 940.

[2] B. B. Smith and D. T. Sawyer, *Inorg. Chem.*, 1968, **7**, 922.

[3] A. G. Sykes and J. A. Weil, *Progr. Inorg. Chem.*, 1970, **13**, 76.

of the binuclear μ-hydroxo-complex. To establish the conditions for complete hydrolysis of the μ-hydroxo-complex, and the stability of the mononuclear product, we studied briefly various aspects of the solution chemistry of these complexes, including in particular the kinetics of the hydrolysis reaction, as reported in the first part of this paper. The remainder is mainly concerned with studies of the reactions of $[Co(nta)(OH_2)_2]$ with various non-metallic ions or molecules.

RESULTS

Acid Hydrolysis of the μ-Hydroxo-complex $[Co_2(nta)_2(OH)_2]^{2-}$.—Because of the low solubility of the potassium salt (Mori's α form) we used solutions of the corresponding sodium salt for kinetic experiments. This complex was obtained directly as the solid, $Na_2[Co_2(nta)_2(OH)_2]{\cdot}4H_2O$, and also in solution by double decomposition from the corresponding potassium salt. Preliminary experiments showed a difference in the kinetic behaviour on acidifying aqueous solutions of the μ-hydroxo-complex obtained in these two ways. When solutions of the solid sodium salt were brought to pH *ca.* 2, a rapid, but not instantaneous, colour change from blue to purple was observed. Repeated spectrophotometric scans of the spectra (300—600 nm) of such solutions showed that further slow changes in absorbance were occurring. Similar rapid changes were observed on acidification of solutions prepared from the potassium salt, but changes in absorbance associated with the subsequent slow reaction were much smaller than those obtained with acidified solutions of the solid sodium salt. The magnitudes of the absorbance changes for the slow reaction varied from one preparation of the solid sodium salt to another, but in all cases, including solutions prepared from the potassium salt, final spectra were identical with that obtained from an acidified solution of the mononuclear complex $K[Co(nta)(OH)(OH_2)]{\cdot}2H_2O$ prepared from the purified β form. We conclude that two isomeric forms of the binuclear complex are formed. Accepting that it is of the di-μ-hydroxo-type, the two nitrogen atoms, the μ-hydroxo-groups, and the two cobalt atoms must all lie in the same plane. Isomers can arise through alternative relative positions for the nitrogen atoms; they may lie either on the same side of the line joining the cobalt atoms (*cis*-isomer), or on opposite sides (*trans*-isomer).

Approximate values for the rate constant for the rapid hydrolysis reaction were obtained spectrophotometrically at 340 nm. Solutions were prepared by double decomposition from the potassium salt since this material appeared to contain a high proportion of the more rapidly reacting isomer. At 25·0 °C, ionic strength $I = 1{\cdot}00\text{M}$ ($NaClO_4$), and *ca.* 4mM-$[Co_2(nta)_2(OH_2)]^{2-}$, optical-density measurements over three half-lives showed that the reaction was first order in the complex concentration, the velocity constant being $0{\cdot}35 \pm 0{\cdot}05$, $0{\cdot}135 \pm 0{\cdot}024$, and $0{\cdot}047 \pm 0{\cdot}005\ s^{-1}$ at $[H^+] = 20{\cdot}0$, 8·0, and 3·0mM, respectively.* We note that this reaction is approximately first order in $[H^+]$.

The slower reaction was investigated in more detail by using solutions of the solid sodium salt of the binuclear complex. This reaction also was followed spectrophotometrically at 340 nm. At a given pH the rate of the faster reaction is *ca.* 100 times that of the slower reaction, so that the former was complete before readings were taken. Plots of log $(D_t - D_\infty)$ against t, where D_t and D_∞ are optical densities at times t and at the end of the reaction, respectively, were linear for at least three half-lives; values of the first-order velocity constant $k_{obs.}$ obtained from such plots are given in Table 1. The order of the reaction in $[H^+]$ exceeded unity, and $k_{obs.}$ was fitted to expressions (1) and (2). From the best values of a and b

$$k_{obs.} = a[H^+] + b[H^+]^2 \qquad (1)$$

$$k_{obs.} = a[H^+]^2/(b + [H^+]) \qquad (2)$$

so obtained, $a = 0{\cdot}088 \pm 0{\cdot}007\ l\ mol^{-1}\ s^{-1}$ and $b = 0{\cdot}14 \pm 0{\cdot}04\ l^2\ mol^{-2}\ s^{-1}$ for (1), and $a = 0{\cdot}131 \pm 0{\cdot}005\ l\ mol^{-1}\ s^{-1}$ and $b = 0{\cdot}0110 \pm 0{\cdot}0010\ mol\ l^{-1}$ for (2), the appropriate equation was used to calculate values of $k_{obs.}$ at each hydrogen-ion concentration shown in Table 1. The relative standard deviation of the calculated values of $k_{obs.}$ is 21·7% if equation (1) is used and 11·5% for (2). A mechanism which would lead to a kinetic equation of the form of (2) is equations (3) and (4), provided that the singly

$$[(nta)Co(\mu\text{-}OH)_2Co(nta)]^{2-} \underset{k_{-1}}{\overset{k_1[H^+]}{\rightleftharpoons}} [(H_2O)(nta)Co(\mu\text{-}OH)Co(nta)(OH_2)]^- \qquad (3)$$

$$[(H_2O)(nta)Co(\mu\text{-}OH)Co(nta)(OH_2)]^- \xrightarrow{k_2[H^+]} 2[Co(nta)(OH_2)_2] \qquad (4)$$

bridged intermediate is present in very small concentrations. In this case $a = k_1$ and $b = k_{-1}/k_2$ in equation (2). It is possible to suggest a plausible mechanism which would lead to a kinetic law of the form of (2) if the binuclear complex involves a single oxo-bridge. Hence, the establishing of this rate law does not constitute a proof of the di-μ-hydroxo-formulation of this complex.

TABLE 1

Velocity constants for hydrolysis of $[Co_2(nta)_2(OH)_2]^{2-}$ (less reactive isomer) at 25 °C and $I = 1{\cdot}00\text{M}$ ($NaClO_4$)

$10^2[H^+]/\text{M}$	$10^3k_{obs.}/s^{-1}$	$10^2[H^+]/\text{M}$	$10^3k_{obs.}/s^{-1}$
32·4	49	5·89	6·3
31·6	54	4·90	5·4
28·2	41	4·07	4·5
26·3	32	3·31	3·1
21·4	29	2·63	1·9
19·6	28	2·04	1·6
17·0	20	1·51	1·2
12·0	13	1·35	0·96
10·5	13	1·23	0·82
8·71	8·8	1·21	0·78
7·76	8·6	0·83	0·49
6·76	7·0	0·81	0·53

Behaviour of Solutions of $[Co(nta)(OH_2)_2]$.—Solutions of the violet complex $[Co(nta)(OH_2)_2]$, prepared both from the solid purified β form and by hydrolysis of the binuclear complex, were titrated with alkali; identical titration curves were obtained. From these curves a value of the first acid dissociation constant of the complex was found to be $pK_1 = 6{\cdot}71 \pm 0{\cdot}01$ at 25·0 °C and $I = 1{\cdot}00\text{M}$ ($NaClO_4$). In dilute solutions, the blue complex $[Co(nta)(OH)(OH_2)]^-$ is fairly stable in the short term, but the green-yellow complex $[Co(nta)(OH)_2]^{2-}$ decomposes relatively rapidly and a satisfactory measurement of pK_2 was not made. Very approximately, $pK_2 = 10$.

At pH 7·5, $[Co(nta)(OH)(OH_2)]^-$ being the dominant species, changes in colour from blue to violet were observed over several hours. The product solution was filtered to remove a small amount of brown precipitate, and brought

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* 1M = 1 mol dm^{-3}.

to pH 1·27. A first-order reaction was then observed spectrophotometrically at 340 nm, the rate constant at 25·0 °C and $I = 1{\cdot}00\text{M}$ ($NaClO_4$) being $5{\cdot}4 \times 10^{-3}\ s^{-1}$. Interpolation of the data in Table 1 gives a value of $5{\cdot}9 \times 10^{-3}\ s^{-1}$ at pH 1·27 for hydrolysis of the more slowly reacting binuclear isomer. It appears that the formation of binuclear complex from $[Co(nta)(OH)(OH_2)]^-$ gives little if any of the more rapidly reacting isomer, since no rapid spectral changes characteristic of the presence of the latter were observed on acidification.

The stability of $[Co(nta)(OH_2)_2]$ in acid solutions was examined. It was found inadvisable to heat acid solutions of the mononuclear complex since some decomposition occurred giving cobalt(II), $2[Co(nta)(OH_2)_2] \longrightarrow [Co(Hnta)_2]^- + Co^{2+}$. At room temperature this reaction was of negligible importance in a period of 24 h at pH 1. The effect of buffers on the spectrum of $[Co(nta)(OH_2)_2]$ was also investigated. Minor changes were observed with the buffer systems H_3PO_4–$[H_2PO_4]^-$, $MeCO_2H$–$MeCO_2^-$, and $[H_2PO_4]^-$–$[HPO_4]^{2-}$, but the system HCO_2H–HCO_2^- caused considerable changes in the region of 340 nm. All these changes took several hours for completion, and are ascribed to slow substitution of a water ligand by the buffer base. Measurements of the final optical density at 340 nm were made for various concentrations of formate ion. If the equilibrium is of the form (5), where in this case L is formate, the corresponding stability constant K_L

$$[Co(nta)(OH_2)_2] + L^{n-} \overset{K_L}{\rightleftharpoons} [Co(nta)(L)(OH_2)]^{n-} \qquad (5)$$

can be obtained from equation (6), where $[Co^{III}]$ is the

$$\frac{[Co^{III}][L]l}{D_L - D_{aq}} = \frac{[L]}{\varepsilon_L - \varepsilon_{aq}} + \frac{1}{K_L(\varepsilon_L - \varepsilon_{aq})} \qquad (6)$$

total concentration of cobalt(III)–nta complexes, D_L is the optical density observed for this value of $[Co^{III}]$ at a concentration [L] of free ligand (formate), D_{aq} is the corresponding optical density in the absence of L, l is the path length of the optical cell, and ε_L and ε_{aq} are the molar absorption coefficients of $[Co(nta)(L)(OH_2)]^{n-}$ and $[Co(nta)(OH_2)_2]$, respectively. From a plot of the left-hand side of (6) against $[HCO_2^-]$, we found $K_L = ca.\ 31\ l\ mol^{-1}$. The measurements showed a substantial difference between the molar absorption coefficients of the parent complex (ε 70) and the formato-complex (ε 42 $l\ mol^{-1}\ cm^{-1}$) at 340 nm; we have no direct evidence whether the smaller absorbance changes observed with other buffers are due to smaller stability constants or to smaller differences in absorption coefficients. In redox reactions of $[Co(nta)(OH_2)_2]$ in $[H_2PO_4]^-$–$[HPO_4]^{2-}$ buffer, slower reactions were observed if the complex and buffer were allowed to stand for several hours before the reducing substrate was added. This we assume to indicate slow substitution of a water ligand by phosphate, the resulting phosphato-complex being less reactive than the diaqua-form. Similar effects were not observed with other buffers. The single case where effects of buffers were observed, even if the substrate was added immediately after the buffer and complex were mixed, occurred in substitution by thiocyanate into the diaqua-complex, a reaction which did not go to completion under our experimental conditions.

Kinetics of Redox and Substitution Reactions of $[Co(nta)(OH_2)_2]$.—The rates of reaction of $[Co(nta)(OH_2)_2]$ in acid solutions were briefly investigated with each of hydrazine, hydroquinone, iodide, nitrite, sulphite, thiocyanate, and thiosulphate. Except for the reaction with sulphite, these reactions were sufficiently slow to be followed by conventional spectrophotometric methods. In most cases measurements were made at or near to 555 nm, a maximum in the spectrum of $[Co(nta)(OH_2)_2]$. The temperature was 25·0 °C and the ionic strength $I = 1{\cdot}00\text{M}$ ($NaClO_4$).

The oxidation of hydrazine was investigated in absence of air, since cobalt(II) catalyses the oxidation of hydrazine by molecular oxygen. Stoicheiometries $S = (\Delta[Co^{III}]/\Delta[\text{Substrate}])$ were measured with $[Co^{III}]_0 = ca.$ 10mM, for concentration ratios $[Co^{III}]_0 : [N_2H_4]_0 = 0{\cdot}46$—$2{\cdot}30 : 1$. (The subscript zero indicates $t = 0$). At pH 3·45, $S = 1{\cdot}14 \pm 0{\cdot}07$; this is consistent with oxidation of the hydrazine to molecular nitrogen plus ammonia. Kinetic results are summarised in Table 2. The first-order velocity constant $k_{obs.}$ was obtained from the gradient of linear plots of log $(D_t - D_\infty)$ against t, where D_t and D_∞ are optical densities at time t and at the end of the reaction. The plots were linear over at least two half-lives.

TABLE 2

Velocity constants for reaction of $[Co(nta)(OH_2)_2]$ with various substrates

pH	[Substrate]/M	$10^3k_{obs}/s^{-1}$
Hydrazine: $[Co^{III}]_0 = 1{\cdot}00$mM, λ = 560 nm		
3·61	0·150	0·296
3·59	0·300	0·616
4·63	0·150	0·765
4·63	0·300	1·65
5·72	0·0375	1·54
5·73	0·0500	1·98
5·72	0·0625	2·45
Hydroquinone: $[Co^{III}]_0 = 1{\cdot}54$mM, λ = 560 nm		
3·51	0·048	0·50
3·51	0·096	0·93
3·49	0·192	1·90
4·53	0·048	0·63
4·55	0·096	1·35
4·52	0·120	1·65
5·91	0·048	5·8
5·89	0·072	8·8
5·90	0·096	11·5
Hydroxylamine: $[Co^{III}]_0 = 1{\cdot}50$mM, λ = 560 nm		
2·37	0·300	0·085
3·33	0·150	0·111
3·36	0·300	0·210
4·72	0·150	0·82
4·75	0·300	1·57
5·97	0·040	11·5
5·96	0·060	18·2
Nitrite (substitution): $[Co^{III}]_0 = 1{\cdot}54$mM, λ = 500 nm		
4·64	0·100	0·275
4·64	0·200	0·816
4·67	0·350	1·83
(redox): $[Co^{III}]_0 = 2{\cdot}00$mM, λ = 560 nm		
5·72	0·0375	5·3
5·73	0·0500	6·8
5·76	0·0625	8·2
Thiocyanate: $[Co^{III}]_0 = 1{\cdot}54$mM, λ = 420 nm		
3·71	0·050	1·01
3·70	0·075	1·25
3·73	0·100	2·02
3·72	0·125	2·12
3·73	0·150	2·80
5·90	0·0250	10·8
5·91	0·0375	11·7
5·89	0·0500	12·4
5·90	0·0625	13·2

TABLE 2 (*Continued*)

Thiosulphate: $[Co^{III}]_0$ = 1·54mM, λ = 555 nm		
4·50	0·050	0·65
4·49	0·150	2·06
4·51	0·300	4·21
5·90	0·0375	6·50
5·89	0·0500	9·91
5·87	0·0625	10·6
Iodide: $[Co^{III}]_0$ = 1·54mM, λ = 555 nm		
1·04	0·050	1·07
2·48	0·025	0·58
2·48	0·050	1·20
2·52	0·150	3·30
2·50	0·390	8·90
3·65	0·025	0·52
3·64	0·033	0·62
3·61	0·040	0·81
3·62	0·050	1·08 [a]
3·64	0·050	1·10
3·60	0·050	1·12
3·63	0·050	1·08 [b]
3·64	0·050	1·05 [c]
3·66	0·050	1·09 [d]
3·61	0·067	1·26
3·63	0·100	2·12
3·62	0·200	4·06
3·64	0·300	5·96
3·63	0·400	8·33
3·61	0·500	9·96
4·73	0·025	0·99
4·72	0·050	2·08
4·73	0·150	5·25
4·74	0·363	11·2
5·97	0·025	7·3
5·99	0·038	10·8
5·98	0·038	10·8 [e]
6·00	0·050	14·8
5·98	0·063	18·4
5·97	0·075	24·5
5·99	0·100	30·7
5·97	0·125	36·3

[a] Reaction conducted under argon. [b] Buffer concentration doubled. [c] $[Co^{III}]_0$ = 3·08mM. [d] I_3^- Production was followed (at 450 nm). [e] 3·75mM-$[Co^{II}(nta)(OH_2)_2]^-$ was present.

Even in the absence of air, the oxidation of hydroquinone to quinone was complicated by the formation of an orange colouration which appeared during the last stages of the reaction. This colouration appeared more rapidly, after *ca.* six half-lives, if air was not excluded, but the optical behaviour and rate of the major part of the reaction were unaffected by the presence of air. To avoid possible errors, Swinbourne's method [4] was used in obtaining the first-order velocity constants shown in Table 2, thus rendering values of D_∞ unnecessary.

With hydroxylamine, $S = 1·20 \pm 0·03$ at $[Co^{III}]_0$ *ca.* 10mM and $[Co^{III}]_0 : [NH_2OH]_0$ = 0·46—2·30 : 1, at pH 3·30. Air did not affect the stoicheiometry or the kinetic behaviour. The nitrogenous products were not investigated, but the value of S suggests that molecular nitrogen predominates. Linear plots of log $(D_t - D_\infty)$ against t were obtained, and the velocity constants so obtained are summarised in Table 2.

Spectrophotometric investigation over the range 450—600 nm of the reaction between $[Co(nta)(OH_2)_2]$ and an excess of iodide showed an isosbestic point at 511 nm which was preserved for five half-lives, and the final spectrum was characteristic of tri-iodide ion. This reaction gave linear plots of log $(D_t - D_\infty)$ against t over at least three half-lives. The system was found convenient for more extensive variations in concentration and other conditions, compared with systems involving the other substrates; first-order velocity constants are summarised in Table 2.

With nitrite as substrate, consistent kinetic results could not be obtained at pH 3·5 or less, probably due to decomposition of nitrous acid. At pH 4·65, preliminary experiments showed that a new stable compound was slowly formed with a maximum at 514 nm (ε 140 l mol^{-1} cm^{-1}). Spectra of solutions which had ceased reacting were identical for nitrite concentrations exceeding *ca.* 0·05M, at a given $[Co^{III}]_0$. Kinetic experiments at 500 nm, where the change in D is large, gave linear plots of log $(D_\infty - D_t)$ against t. The first-order velocity constants so obtained are included in Table 2. At pH 5·74, the system showed the general decrease in light absorption characteristic of reduction of the complex to cobalt(II), which absorbs relatively little light in the visible region of the spectrum. Velocity constants obtained from linear plots of log $(D_t - D_\infty)$ are also included in Table 2.

The substrate thiocyanate showed no reducing properties at either pH 3·72 or 5·90. A slow increase in optical density over a wide band of wavelengths showed ligand substitution was probably occurring. This was incomplete, since D_∞ was increased on increasing the concentration of thiocyanate. Nevertheless, the rate of attainment of equilibrium followed first-order kinetics, plots of log $(D_\infty - D_t)$ against t being linear for at least two half-lives. The values of $k_{obs.}$ so obtained are included in Table 1. By assuming an equilibrium of the form (7), values of K_3 =

$$[Co(nta)(OH_2)_2] + NCS^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Co(nta)(NCS)(OH_2)]^- \quad (7)$$

k_3/k_{-3} were obtained by using equation (6). We found K_3 = 17 l mol^{-1} at pH 3·72 ($[NCS^-]$ = 0·050—0·150, $[HCO_2^-]$ = 0·008M), and 23 l mol^{-1} at pH 5·90 ($[NCS^-]$ = 0·025—0·0625, $[HPO_4^{2-}]$ = 0·012M).

Kinetic experiments with thiosulphate as substrate were restricted to pH 4·50 and 5·89; in solutions of lower pH a precipitate of sulphur was formed, greatly restricting the measurable amount of reaction. Even at the pH values cited, reduction of the cobalt(III) complex could not be followed to completion because of the slow formation of a precipitate involving $[Co^{II}(nta)(OH_2)_2]^-$ and thiosulphate. Swinbourne's method [4] was used for obtaining values of $k_{obs.}$ (Table 2), and the reaction was followed for 1—2 half-lives only. It was not possible to determine the stoicheiometry of this reaction satisfactorily.

The stoicheiometry S of the rapid reduction of $[Co(nta)(OH_2)_2]$ by sulphite was determined in the absence of air at pH 3·90 and 6·70. At both pH values, little variation in S was found for changes in the ratio $[Co^{III}]_0/[SO_3^{2-}]_0$ from 0·4 to 3·5, with $[Co^{III}]_0$ = *ca.* 14mM. The order of mixing the reagents did not affect S, as sometimes occurs with rapid reactions. At 25·0 °C, $S = 1·52 \pm 0·03$ (pH 3·90) and $1·51 \pm 0·03$ (pH 6·70). Two experiments at 8mM-Cu^{2+} gave S = 1·91 (pH 3·90). These results indicate that dithionate and sulphate are probable products of the reaction. A preliminary investigation of the reaction by stopped-flow spectrophotometry showed complicated kinetic behaviour. At pH 6·20 with $[Co^{III}]_0$ = 5·4—9·2mM, the rate of reaction was unaffected by varying the sulphite concentration in the range 60—200mM. A mild retardation was observed when $[Co^{II}(nta)(OH_2)_2]^-$ was added and plots of log $[Co^{III}]_t$ against t showed curvature, the

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[4] E. S. Swinbourne, *J. Chem. Soc.*, 1960, 2371.

(negative) gradient decreasing with t. The first-order velocity constant obtained from the initial gradient of such plots was *ca.* 16 s^{-1} at 30·0 °C and $I = 1{\cdot}00\text{M}$ ($NaClO_4$). At pH 1·60, under which conditions $[Co^{II}(nta)(OH_2)_2]^-$ is decomposed to Co^{2+}, linear plots of $\log [Co^{III}]_t$ against t were obtained, and the velocity constant was *ca.* 0·6 s^{-1} at a sulphite concentration of 200mM, 30·0 °C, and $I = 1{\cdot}00\text{M}$ ($NaClO_4$).

DISCUSSION

The results in Table 2 show that for the majority of substrates, the first-order velocity constant is proportional to the substrate concentration over the ranges investigated, at a fixed pH. The corresponding second-order velocity constants, $k_4 = k_{\text{obs.}}/[\text{Substrate}]$, are summarised in Table 3. The value of k_4 for the redox reaction involving nitrite at pH 5·74 was obtained in this way, but the ligand-substitution by nitrite at pH 4·65 shows a dependence of $k_{\text{obs.}}$ on $[NO_2^-]$ exceeding unity. Because the product spectrum is independent of $[NO_2^-]$ over the concentration range recorded, we have assumed that this product is $[Co^{III}(nta)(NO_2)_2]^{2-}$, and that the order in nitrite can be interpreted by the two-stage process (8) and (9). If the stationary-state

$$[Co(nta)(OH_2)_2] + NO_2^- \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} [Co(nta)(NO_2)(OH_2)]^- \quad (8)$$

$$[Co(nta)(NO_2)(OH_2)]^- + NO_2^- \xrightarrow{k_6} [Co(nta)(NO_2)_2]^{2-} \quad (9)$$

approximation can be applied to the concentration of mononitro-complex, we obtain (10) by means of which we find $k_5 = 8{\cdot}8 \times 10^{-3}$ l mol^{-1} s^{-1} and $k_{-5}/k_6 = 0{\cdot}8$

$$k_{\text{obs.}} = k_5k_6[NO_2^-]^2/(k_{-5} + k_6[NO_2^-]) \quad (10)$$

mol l^{-1} from the values of $k_{\text{obs.}}$ at pH 4·65. This value of k_5 is included in Table 3.

TABLE 3

pH Dependence of velocity constants, 10^2k/l mol^{-1} s^{-1}, for the reaction of $[Co(nta)(OH_2)_2]$ with various substrates at 25 °C and $I = 1{\cdot}00\text{M}$ ($NaClO_4$)

Substrate \ pH(approx.)	2·4	3·5	4·7	5·9
Hydrazine		0·20 ±0·01	0·53 ±0·02	40 ±1
Hydroquinone		1·00 ±0·04	1·37 ±0·04	12·1 ±0·1
Hydroxylamine	0·028 ±0·002	0·072 ±0·002	0·54 ±0·02	29·6 ±0·1
Iodide	2·30 ±0·09	2·07 ±0·11	3·68 ±0·48	29·8 ±1·3
Nitrite			0·88 ±0·09	13·6 ±0·6
Thiocyanate		*ca.* 2		*ca.* 6
Thiosulphate			1·36 ±0·06	17·7 ±1·0

The values of $k_{\text{obs.}}$ for substitution by thiocyanate have been interpreted in terms of equilibrium (7) which leads to the relation $k_{\text{obs.}} = k_3[NCS^-] + k_{-3}$. By using this equation we have obtained the k_3 values recorded in Table 3 from the $k_{\text{obs.}}$ values in Table 2. Values of K_3 calculated from k_3 and k_{-3} are not in good agreement with those obtained from the optical densities of equilibrated mixtures of thiocyanate and $[Co(nta)(OH_2)_2]$. A contributory factor is believed to be the concurrent formation of complexes with the buffer anion, for which we have made no allowance. Hence, the values of k_3 which we have included in Table 3 are likely to be erroneous, as also are values of K_3. However, we consider the values of k_3 are likely to be correct within an order of magnitude, which is sufficient for our purposes.

The velocity constants summarised in Table 3 increase with increase in pH. The substrates iodide and thiosulphate do not undergo proton-transfer equilibria under the conditions of our experiments, and we ascribe the change in k to different rate constants, k_a and k_b, for the reaction of $[Co(nta)(OH_2)_2]$ and its conjugate base $[Co(nta)(OH)(OH_2)]^-$, respectively, with these substrates. By using the appropriate equation (11) we

$$k = \{k_a[H^+]/(K_1 + [H^+])\} + \{k_bK_1/(K_1 + [H^+])\} \quad (11)$$

have analysed the k values for these substrates (Table 3) to obtain k_a and k_b (Table 4). The previously determined value of $K_1 = 1{\cdot}95 \times 10^{-7}$ mol l^{-1} was used for the first acid-dissociation constant of $[Co(nta)(OH_2)_2]$. The treatment for thiocyanate is similar, but the uncertainty about values of k for this substrate renders k_a and k_b very tentative. With nitrite, the value of k_b, which depends mainly on the experimental results at pH 5·74 for the redox reaction, is fairly reliable, but the value for k_a is less certain since it derives mainly from results at pH 4·65 which are the subject of a debatable interpretation. Equation (11) was also used to evaluate k_a and k_b values for hydroquinone. A term showing the same dependence on $[H^+]$ as the term in k_b would arise if reaction between p-$C_6H_4(OH)O^-$ and $[Co(nta)(OH_2)_2]$ is a contributory path. However, the ionisation of hydroquinone is small at the pH of our experiments ($pK_1 \approx 10$), and we have assumed that the k_b term is entirely due to reaction between un-ionised hydroquinone and the conjugate base of the complex.

TABLE 4

Approximate values of velocity constants for reactions between $[Co(nta)(OH_2)_2]$ (k_a) or its conjugate base (k_b) and various substrates

Substrate	10^2k_a/l mol^{-1} s^{-1}	10^2k_b/l mol^{-1} s^{-1}
$[N_2H_5]^+$	0·16	<46
N_2H_4	<640	
$C_6H_4(OH)_2$	0·82	86
$[NH_3OH]^+$	0·022	<120
NH_2OH	<26	420
I^-	2·17	164
$[NO_2]^-$	(<0·88)	140
$[NCS]^-$	(*ca.* 2)	(*ca.* 30)
$[S_2O_3]^{2-}$	0·50	120

The dependence on the hydrogen-ion concentration of k for the reaction involving hydroxylamine cannot be described satisfactorily by equation (11). We have assumed that reactions involving both hydroxylamine and its conjugate acid must be taken into account. In the general case, if K_s is the acid-dissociation constant of a substrate, we have equation (12) where $Q = (K_s + [H^+])(K_1 + [H^+])$. The terms in k_d and k_e show the

$$k = (k_c[H^+]^2/Q) + (k_dK_s[H^+]/Q) + (k_eK_1[H^+]/Q) + (k_fK_sK_1/Q) \quad (12)$$

same dependence on hydrogen-ion concentration, and so cannot be distinguished by kinetic measurements. Upper limits can be obtained for k_d and k_e by assuming that the complementary constant, k_e or k_d, respectively, is zero. This procedure has been used in fitting the results for hydroxylamine in Table 3 to equation (12). The previously quoted value of K_1 was used, together with $K_s = 8{\cdot}7 \times 10^{-7}$ mol l^{-1} for hydroxylammonium ion.[5] The derived constants are included in Table 4, k_c and k_d under the heading k_a, since they refer to reactions of $[Co(nta)(OH_2)_2]$; k_e and k_f, which refer to reactions of $[Co(nta)(OH)(OH_2)]^-$, are under the heading k_b. We might expect a similar situation to arise with hydrazine, but no evidence was found for a term in k_f. Hydrazine is 60 times more basic than hydroxylamine ($K_s = 1{\cdot}35 \times 10^{-8}$ mol l^{-1} at 30 °C for hydrazinium ion [5]), and a higher pH than 5·7 may be required before k_f contributes significantly to k. In principle, terms in both k_d and k_e may arise, and therefore upper limits are quoted for these constants.

Considering the velocity constants summarised in Table 4, we note the numerical similarity between the k_a values for reactions of the various substrates with $[Co(nta)(OH_2)_2]$, although two reactions are of different type from the remainder. We note also that the conjugate base of the cobalt(III) complex reacts more rapidly than the diaqua-form with a given substrate. Hence, we consider that even with the redox reactions the rate-limiting step is a ligand substitution, involving replacement of the ligand water by a substrate species. The similarity of the velocity constants suggests that this process is essentially of the dissociative type. This being so, the value of $k_a = 6{\cdot}4$ l mol^{-1} s^{-1} for reaction between $[Co(nta)(OH_2)_2]$ and N_2H_4 seems unduly high, especially as no reaction between $[Co(nta)(OH)(OH_2)]^-$ and N_2H_4 was detected. We suggest that this value should be disregarded as too large, and in consequence that a value of *ca.* 0·46 l mol^{-1} s^{-1} is acceptable for the reaction between $[Co(nta)(OH)(OH_2)]^-$ and $[N_2H_5]^+$. Similarly, although the argument is less strong, it seems possible that the value $k_a = 0{\cdot}26$ l mol^{-1} s^{-1} for NH_2OH is too high, and therefore that $k_b = 1{\cdot}2$ l mol^{-1} s^{-1} for $[NH_3OH]^+$ is not a serious overestimate.

The original intention of this work was to develop systems using complexes of the type $[Co^{III}(nta)(OH_2)(L)]$, with L as a reducing ligand, in which studies could be made of the mechanism of oxidation of the co-ordinated L. However, our experiments show that the formation of this type of complex from the parent $[Co^{III}(nta)(OH_2)_2]$ is usually a slower step than the subsequent redox reaction. A similar situation has already been found in oxidations involving hexa-aquacobalt(III).[6] In the single case in which $L = SO_3^{2-}$, the substitution step appeared to be more rapid than the subsequent steps, as shown by the lack of dependence of rate on sulphite concentration. The abnormally rapid substitution of ligand water by sulphite in cobalt(III) complexes has been observed previously.[7] The retardation by $[Co^{II}(nta)(OH_2)_2]^-$, and the increase in S when Cu^{2+} is present, may be evidence of the formation of a free radical such as $\cdot SO_3^-$. However, these experiments were not continued because the stopped-flow spectrophotometer available at the time was equipped with a stainless-steel mixing chamber, and rates of reaction were affected to a small extent by the contact time of solutions in this part of the apparatus.

EXPERIMENTAL

Reagents, including substrates, buffers, perchloric acid, and sodium perchlorate, were of AnalaR quality or were prepared from AnalaR materials, with the exceptions of hydrazine hydrate, nitrilotriacetic acid, sodium tetraphenylborate, and sodium thiocyanate which were of ' reagent ' quality. All were used without further purification. Concentrations of stock solutions were established by standard methods.

Preparations of Cobalt(III)*–nta Complexes by Mori's Method.*—The α, β, and ' μ-diol ' cobalt(III)–nta complexes were prepared as their potassium salts as described by Mori *et al.*[1] We confirmed the majority of the conclusions [2] of Smith and Sawyer about the formulation of these complexes. α Form {Found: C, 21·6; H, 2·5; Co, 16·4; K, 10·2; N, 4·2. $K_2[Co_2(nta)_2(OH)_2]\cdot 6H_2O$ requires C, 20·2; H, 3·7; Co, 16·5; K, 11·0; N, 3·9%}: maxima and molar absorption coefficients in the visible spectrum were at 568 (ε 296) and 397 nm (ε 395 l mol^{-1} cm^{-1}). Successive preparations of the β form gave samples of different, although similar, composition, a typical analysis (Found: C, 21·1; H, 2·9; Co, 15·8; K, 10·5; N, 3·7%) showing a Co : nta ratio near to unity. The material was a mixture of cobalt(II) and cobalt(III) compounds; the above sample contained 10·7% of cobalt(III), as shown by dissolving a portion in an excess of standard acidified $FeSO_4$ solution and titrating the remaining Fe^{2+} with a standard Ce^{IV} solution. Repeated extraction of the β form with aqueous methanol gave a red extract and left a blue solid which we identified as a mononuclear cobalt(III)–nta complex {Found: C, 21·8; H, 2·7; Co, 16·5; K, 10·1; N, 4·5. $K[Co(nta)(OH)(OH_2)]\cdot 2H_2O$ requires C, 20·2; H, 3·7; Co, 16·5; K, 11·0; N, 3·9%}. This material, although giving very similar analysis figures to the binuclear β form, is distinct, as shown by differences in visible spectra and solubility. Maxima and molar absorption coefficients in the visible spectra of the purified β complex were: at pH 3·5, 555 (ε 129) and 399 (ε 124); at pH 5·9, 560 (ε 117), and 395 (ε 111); at pH 8·2, 570 (ε 106) and 385 nm (ε 102 l mol^{-1} cm^{-1}). The ' μ-diol ' gave analysis figures showing it to be a bis(nta) complex, but the atomic ratio K : Co was 0·54 : 1. Recrystallisation from KCl solution gave a purer product {Found: C, 29·9; H, 2·8; Co, 11·4; K, 7·6;

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[5] ' Stability Constants of Metal–Ion Complexes,' Supplement No. 1, *Chem. Soc. Special Publ.*, No. 25, 1971.

[6] G. Davies and K. O. Watkins, *J. Phys. Chem.*, 1970, **74**, 3388.

[7] R. S. Murray, D. R. Stranks, and J. K. Yandell, *Chem. Comm.*, 1969, 604.

N, 5·9. $K[Co(Hnta)_2]\cdot 2H_2O$ requires C, 28·1; H, 3·5; Co, 11·5; K, 7·6; N, 5·5%}.

Preparation of $Na_2[Co_2(nta)_2(OH)_2]\cdot 4H_2O$.—Solid nitrilotriacetic acid (4·0 g) was dissolved in a solution of $NaHCO_3$ (5·0 g) in water (20 cm³). Solid $CoCl_2\cdot 6H_2O$ (5·0 g) was then added, the solution was heated to 50 °C, and 30% H_2O_2 solution (7·5 cm³) was slowly added with stirring, pH 8—9 being maintained by the further addition of solid $NaHCO_3$. The solution was filtered, methanol (10 cm³) was added, and the mixture was cooled to *ca.* 0 °C and left overnight. The resulting precipitate was filtered off, washed with ice-cold methanol, and dried by suction {Found: C, 22·5; H, 2·5; Co, 18·1; N, 4·3. $Na_2[Co_2(nta)_2(OH)_2]\cdot 4H_2O$ requires C, 22·3; H, 3·4; Co, 18·2; N, 4·3%}. The visible spectrum of this salt, containing the two isomers, is similar to that of the potassium salt (α complex) as given by Mori *et al.*[1]

Preparation of a Cobalt(II)*-nta Complex.*—Solid nitrilotriacetic acid (4·0 g) was dissolved in a solution of $KHCO_3$ (5·1 g) in water (20 cm³). Solid $CoCl_2\cdot 6H_2O$ (5·0 g) was added, and the mixture was warmed with stirring until a solution was obtained. Methanol (*ca.* 20 cm³) was added, and the solution was cooled, resulting in rapid crystallisation. The crystals were filtered off, washed with methanol, and dried by suction {Found: C, 25·0; H, 3·1; Co, 18·6; K, 12·3; N, 4·4. $K[Co(nta)(OH_2)_2]$ requires C, 22·4; H, 3·1; Co, 18·3; K, 12·1; N, 4·4%}. A maximum in the visible spectrum occurred at 515 nm (ε 21·1 l mol⁻¹ cm⁻¹). At 555 and 560 nm, the wavelengths used for most of the kinetic experiments involving reduction of the cobalt(III) complex by a substrate, the molar absorption coefficients of this cobalt(II) complex are *ca.* 1 l mol⁻¹ cm⁻¹. The red solid obtained by addition of methanol to the aqueous methanolic extract from the β-complex gave a closely similar spectrum.

Determination of pK_1 *for* $[Co^{III}(nta)(OH_2)_2]$.—pH-Titration curves were obtained by using Radiometer automatic-titration equipment, both with the mononuclear cobalt(III) complex obtained from the β complex and with solutions of this complex obtained by prior treatment of the α complex with dilute acid. Identical results were obtained; at 25·0 °C and $I = 1{\cdot}00\text{M}$ ($NaClO_4$), p$K_1 = 6{\cdot}71 \pm 0{\cdot}01$. Titration of $Na_2[Co_2(nta)_2(OH)_2]\cdot 4H_2O$ gave the anomalous curve, characteristic of hydrolysis to mononuclear species, of a μ-hydroxo-complex.[8]

Redox Potential of the Couple $[Co^{III}(nta)(OH_2)_2]$–$[Co^{II}(nta)(OH_2)_2]^-$.—The method described previously was used.[9] Concentrations of the Co^{III} and Co^{II} complexes were 0·50—2·00 and 1·00mM, respectively. Buffer concentrations were 15mM-acetate and 48mM-phosphate, respectively, and $I = 1{\cdot}00\text{M}$ ($NaClO_4$) at 25·0 °C. At pH 4·54 (acetate buffer) $E^\ominus = 0{\cdot}717$, and at pH 5·70 (phosphate buffer) $E^\ominus = 0{\cdot}692$ V. These values are similar to that for the diaquadioxalato-complexes of cobalt ($E^\ominus$ 0·78 V) and considerably higher than that for the ethylenediaminetetra-acetato-complexes ($E^\ominus$ 0·38).[9]

Kinetic Experiments on the Hydrolysis of $[Co_2(nta)_2(OH)_2]^{2-}$.—A solution of the rapidly reacting isomer was prepared by stirring an excess of finely ground $K_2[Co_2(nta)_2(OH)_2]\cdot 6H_2O$ with a solution of sodium tetraphenylborate, and filtering off the remaining solid potassium complex and the precipitated potassium tetraphenylborate. *Ca.* 0·1 cm³ of this solution (*ca.* 0·1M in the binuclear complex) was injected by Nylon syringe into 3·0 cm³ of a solution of known concentration of perchloric acid of $I \approx 1{\cdot}0\text{M}$ ($NaClO_4$) contained in a 1·0 cm optical cell closed with a rubber septum, and placed in the temperature-controlled cell holder of a Unicam SP 800B spectrophotometer. The syringe contained air above the solution of complex, so that by completing the travel of the piston the air was forced through the solution in the cell, effecting complete mixing. The optical density of the solution at 340 nm was measured on a Unicam SP 20 pen recorder, the chart of which was set in motion before mixing. The approximate rates of reactions of half-life as low as *ca.* 2 s could be measured in this way.

The hydrolysis of the more slowly reacting isomer was followed at 340 nm by using solutions of the solid complex $Na_2[Co(nta)(OH_2)_2]\cdot 4H_2O$. Appropriate volumes of perchloric acid and of the complex were mixed, and a sample of the mixture was placed in a 2·0 cm optical cell of a Uvispek H700 manual spectrophotometer fitted with a temperature-controlled cell holder. The ionic strength of both solutions was 1·00M ($NaClO_4$). In experiments at pH <0·8, the more rapid reactions made it necessary to mix the reactant solutions by syringe in the cell itself. The sum of the concentrations of the slowly and rapidly reacting binuclear complexes was *ca.* 2mM; with these techniques, the more labile isomer had hydrolysed before the first measurement of optical density. The Uvispek H700 was also used to measure optical densities of $[Co(nta)(OH_2)_2]$ solutions in formate buffers, after equilibrium had been reached. The qualitative investigation of the effect of buffers on $[Co(nta)(OH_2)_2]$ was made by scanning the spectrum of this complex at appropriate intervals of time using the SP 800B spectrophotometer.

Kinetic Experiments on the Reaction of $[Co(nta)(OH_2)_2]$ *with Various Substrates.*—Solutions of the mononuclear complex were prepared by dissolving $Na_2[Co_2(nta)_2(OH)_2]\cdot 4H_2O$ in 0·185M-$HClO_4$, and allowing the solution to stand overnight. All experiments were made at 25·0 °C and $I = 1{\cdot}00\text{M-}NaClO_4$ with the following buffers present: H_3PO_4–$[H_2PO_4]^-$ (2·3—2·5); HCO_2H–HCO_2^- (3·3—3·8); $MeCO_2H$–$MeCO_2^-$ (4·5—4·8); and $[H_2PO_4]^-$–$[HPO_4]^{2-}$ (pH 5·7—6·0). The concentration of the acid plus base constituents of the buffer was *ca.* 0·015M, except for $[H_2PO_4]^-$–$[HPO_4]^{2-}$ which was *ca.* 0·024M. Preliminary kinetic experiments were made by repeatedly scanning the region 400—600 nm with the Unicam SP 800B spectrophotometer; this enabled an appropriate choice of wavelength to be made for further experiments. The more rapid reactions, particularly those at pH *ca.* 6, were followed on the Uvispek H700 spectrophotometer, in a similar manner to the hydrolysis reaction described above. Solutions for slower reactions were mixed in a thermostat, and a sample was transferred to a 4·0 cm optical cell in the temperature-controlled cell holder of a Unicam SP 600 spectrophotometer. Measurements of pH of reaction solutions were made at the end of the reaction, using a Radiometer type PHM26 meter. For use with solutions containing perchlorate, the saturated KCl of the calomel reference electrode was replaced by saturated NaCl. In all cases, the meter was standardised with a solution containing 10·0mM-$HClO_4$ and 0·99M-$NaClO_4$, to which a pH of 2·00 was assigned. Stoicheiometries required for the redox systems were obtained by determining the excess of

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[8] A. W. Adamson, H. Ogata, J. Grossman, and R. Newbury, *J. Inorg. Nuclear Chem.*, 1958, **6**, 319.

[9] Lee Hin-Fat and W. C. E. Higginson, *J. Chem. Soc.* (*A*), 1967, 298.

cobalt(III) spectrophotometrically, or, if the substrate was in excess, the amount of it remaining was found by an appropriate titration. No correction was made to values of $k_{obs.}$ in Table 2 to allow for the different stoicheiometries of the various redox reactions studied.

Preliminary measurements of the rate of reaction between $[Co(nta)(OH_2)_2]$ and sulphite were made at 560 nm and 30·0 °C using a stopped-flow spectrophotometer designed and built by Dr. J. R. Chipperfield, to whom we are grateful for offering this facility and for advice.

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